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# Evidence of quasi-intramolecular redox reactions during thermal decomposition of ammonium hydroxodisulphitoferriate(III), (NH$_4$)$_2$[Fe(OH)(SO$_3$)$_2$]·H$_2$O

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## Abstract

Synthesis of ammonium hydroxodisulfitoferriate(III), (diammonium *catena*-{bis(μ$^2$-sulfito-κO,κO)-μ$^2$-hydroxo-κ$^2$O}ferrate(III) monohydrate) (NH$_4$)$_2$[Fe(OH)(SO$_3$)$_2$]·H$_2$O (compound **1**) and its thermal behavior is reported. The compound is stable in air. Its thermal decomposition proceeds without the expected quasi-intramolecular oxidation of sulfite ion with ferric ions. The disproportionation reaction of the ammonium sulfite, formed from the evolved NH$_3$, SO$_2$ and H$_2$O in the main decomposition stage of **1,** results in the formation of ammonium sulfate and ammonium sulfide. The ammonium sulfide is unstable at the decomposition temperature of **1** (150°C) and transforms into NH$_3$ and H$_2$S which immediately forms elementary sulfur by reaction with SO$_2$. The formation and decomposition of other intermediate compounds like (NH$_4$)$_2$S$_n$O$_x$ (n = 2, x = 3 and n = 3, x = 6) results in the same decomposition products (S, SO$_2$ and NH$_3$). Two basic iron sulfates, formed in different ratios during synthesizing experiments performed under N$_2$ or in the presence of air, have been detected as solid intermediates which contain ammonium ions. The final decomposition product was proved to be α-Fe$_2$O$_3$ (mineral name hematite).

## Introduction

In continuation of our efforts to synthesize and study compounds containing redox active anionic and cationic components reacting with each other during heating in quasi-intramolecular redox reactions [1,2], we have synthesized the diammonium *catena*-{bis($\mu^2$-sulfito-$\kappa$O,$\kappa$O)-$\mu^2$-hydroxo-$\kappa^2$O}ferrate(III) monohydrate (*i.e.*, ammonium disulfitohydroxoferriate, chemical formula $(NH_4)_2[Fe(OH)(SO_3)_2]\cdot H_2O$, abbreviated throughout the paper as compound **1**. Its thermal decomposition process and decomposition products were studied by TG-MS, XRD, IR, Raman and Mössbauer spectroscopy. The compound **1** was prepared by Erämetsä and Valkonen [3] first, however, the characterization of the reaction product was limited, and the thermal properties were not known at all. Therefore, the compound **1** was synthesized; for pure material, the thermally initiated decomposition and the identity of decomposition intermediates were investigated.

## Experimentals

As insert for the synthesis experiments served the chemical grade Sigma-Aldrich products iron(III)-chloride hexahydrate and 25 % aqueous ammonia solution. In addition, liquified $SO_2$ in 99.9 % purity was supplied in a pressurized bottle by Unikén Ltd., Kecel, Hungary.

The synthesis of compound **1** was performed by the reaction of freshly prepared FeO(OH) with $SO_2$ in the presence of concentrated aqueous ammonia solution at 60°C [3]. The formed product, however, always contained impurities. The reason for the by-product formation is assigned to the local overheating of the reaction mixture (65-70°C) due to the exothermic reaction of the excess of ammonia and sulfur dioxide gas; thus the method was slightly modified. A long vertical tube equipped with gas inlet and outlet tubes was filled with 50 ml of a 4 M $FeCl_3$ solution, which was mixed with 100 ml of 25 % aqueous $NH_3$ under vigorous stirring when a dark brown precipitate was formed. The mixture was warmed to 50°C; $SO_2$ gas was simultaneously blown into the suspension. As soon as a white ammonium sulfite smoke leaked, the assition of the gas was interrupted. This procedure was repeated several times until any escape of smoke stopped. Then the gas was blown in again, the temperature was not allowed to exceed 60°C, and the mixture was shaken intensively. If the temperature started decreasing, it was adjusted to 60°C by gentle heating. The $SO_2$ insufflation was continued until the whole mixture became egg-yellow in color and the dark brown iron-oxide hydroxide completely disappeared. The mixture was quickly filtered in air and the reaction product was dried in a vacuum desiccator over $P_2O_5$. Due to the creamy character of the freshly prepared product, the drying process in the open air took a long time; after 15-20 minutes of drying, a brown layer of the decomposition product appeared on the surface. Elemental compositions of the starting material and decomposition intermediates (Fe and S content) were determined by ICP-AES with an AtomScan 25 instrument (Thermo Jarrel Ash, USA).

FT-IR spectra of solid samples were recorded in the attenuated total reflection (ATR) mode on a Bruker Alpha FT-IR spectrometer at 2 cm$^{-1}$ resolution.

X-ray powder diffraction measurements were performed using a Philips PW-1050 Bragg-Brentano parafocusing goniometer. It was equipped with a Cu tube operated at 40 kV and 35 mA tube power, a secondary beam graphite monochromator and a proportional counter. Scans were recorded in step mode. Evaluation of the diffraction patterns had been obtained by full profile fitting techniques. Thermal data were collected using TA Instruments SDT Q600 thermal analyzer coupled to Hiden Analytical HPR-20/QIC mass spectrometer. The decomposition was followed from room temperature to 780 °C at 5 °C min$^{-1}$ heating rate in argon and air as carrier gas (flow rate = 50 cm$^3$ min$^{-1}$). Sample holder / reference: alumina crucible / empty alumina crucible. Sample mass ~ 7 mg. Selected ions between $m/z$ = 1–120 were monitored in Multiple Ion Detection Mode (MID).

The Raman measurements were performed using Horiba Jobin-Yvon LabRAM-type microspectrometer with external 532 nm Nd-YAG laser source (~40mW) and Olympus BX-40 optical microscope. The laser beam was focused by an objective of 10×. A D1 intensity filter decreased the laser power to 10 % to avoid the thermal degradation. The confocal hole of 1000 μm and 1800 groove mm$^{-1}$ grating monochromator were used in a confocal system and for light dispersion. The spectral range of 100-4000 cm$^{-1}$ was detected as the relevant range with 3 cm$^{-1}$ resolution. Each spectrum was collected 240 s per point.

The Mössbauer spectra were measured at room temperature using a Mössbauer spectrometer (Ranger) in constant acceleration mode with a $^{57}$Co(Rh) source of 0.2 GBq activity. Isomer shifts are given relative to an alpha-iron at room temperature. The Mössbauer spectra were analyzed assuming Lorentzian line shapes with the help of the Mosswinn 3.0i XP software.

**Results and Discussions**

*Synthesis and properties*

The compound **1** was prepared by a slightly modified method as suggested by Erämetsä and Valkonen [3] based on the reaction of 4 M FeCl$_3$, 25 % aq. NH$_3$ and SO$_2$ gas at 60°C. The thus obtained compound **1** was proved to be sufficiently pure, while the compound **1a** obtained by the original method always contained further ammonium iron sulfite impurities. Avoidance of overheating due to the reaction heat was a key parameter in the preparation of the pure sample. There are good correlations between the powder XRD and IR data for the compound $(NH_4)_2Fe(OH)(SO_3)_2$ given by Erämetsä and Valkonen [3] and our results for compound **1**, but some further characteristics of the data of the impure sample differ. Most conspicuous is the incorporation of solvate water that was missing by the earlier authors. Consequently, the chemical formula has to be changed to $(NH_4)_2Fe(OH)(SO_3)_2 \cdot H_2O$.

Erämetsä and Valkonen [3] gave an orthorhombic unit cell that could be proved during the present work. However, the earlier given cell parameter resulted in a too large unit cell volume with a cell content Z = 5 instead of Z = 4 (Table 1). The XRD peak positions of the compound **1** (Fig. S1) agreed well with the data of [3]. The cell parameters are given in Table 1.

The Mössbauer spectrum of compound **1** with isomer shift, $\delta$=0.392(1) mm s$^{-1}$ and quadrupole splitting, $\Delta$=0.784(1) mm s$^{-1}$ (Fig. 1) is consistent with an octahedral oxygen coordinated high-spin iron(3+) species. A minor (8%) impurity component has not been identified. From these parameters, the polymeric nature of the compound with bridging sulfito or hydroxo groups has to be supposed instead of the S-bound monodentate coordination mode [3].
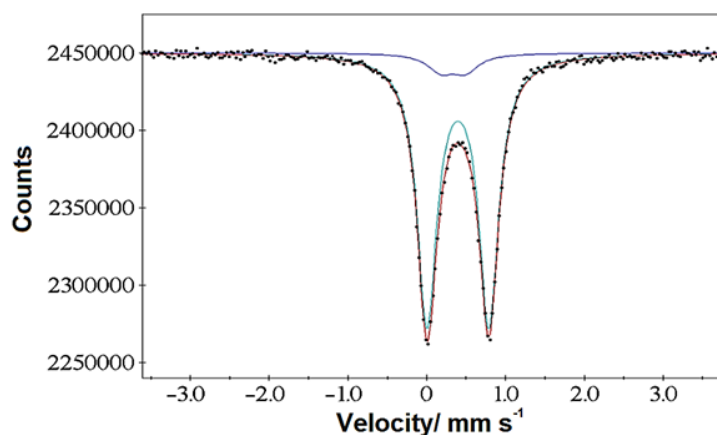


Figure 1. Mössbauer spectrum of compound **1** at room temperature.

The infrared bands of compound **1** (Fig. S2.) agreed well with the data compiled by Erämetsä and Valkonen [3] for $(NH_4)_2Fe(OH)(SO_3)_2$. All four normal modes of the trigonal pyramidal sulfite ion, *i.e.*, $\nu_3(E)$, $\nu_1(A_1)$, $\nu_2(A_1)$ and $\nu_4(E)$ [4,5], are observable in the IR spectra of the compound **1** (Fig. S2.). They are tentatively assigned to absorption bands at 822 cm$^{-1}$ ($\nu_1$, S—O), 646 cm$^{-1}$ ($\nu_2$, S—O), 887 and 1017 cm$^{-1}$ ($\nu_3$, S—O, splitting is due to the bridging $\kappa$O,$\kappa$O coordination and the low $C_s$ symmetry of the sulphite ion) and at 505 cm$^{-1}$ ($\nu_4$, S—O).

**Table 1.** Cell parameters of compound **1**.

|  | **This work (powder XRD)** | **Erämetsä and Valkonen [3]** |
|---|---|---|
| crystal system | orthorhombic | orthorhombic |
| *a* [Å] | 17.781 | 8.912 |
| *b* [Å] | 7.375 | 10.677 |
| *c* [Å] | 7.109 | 11.821 |
| V [Å³] | 932.33 | 1124.81 |
| Z | 4 | 5 |
| space group | Cmc2$_1$ | not given |
| d$_{calc}$ [g cm$^{-3}$] | 2.034 | 1.98 (d$_{exp}$=1.91 [3]) |

The deformation bands of the bridged hydroxyl group were assigned at 1123 cm$^{-1}$, while deformation bands of ammonium ion and solvate water appeared at 1443 and 1637 cm$^{-1}$, respectively. The stretching band of OH occurs at 3506 cm$^{-1}$ and the other (stretching and overtones) OH and NH-bands appear around 2862, 2978, 3086 and 3165 cm$^{-1}$, including shoulders. Further overtones/combination bands were observed between 1700 and 2500 cm$^{-1}$.

**Thermal behaviour**

The dry compound **1** was proved to be stable in air inspite of well-known redox reaction between sulfites and iron(III) ions in aq. phases [6] because the bridging sulfite ions link the iron(III) centers into a polymeric chain giving an unusual stability for the compound **1**. As it can be seen in the Fig. S3a and in Table 2, the complete thermal decomposition process in inert atmosphere gave 73.00 % mass loss, which is in good agreement with the formation of $\alpha$-Fe$_2$O$_3$ as final decomposition product (the theoretical value is 72.13 %). In air, this value was 70.46 %. The presence of $\alpha$-Fe$_2$O$_3$ (hematite) as decomposition product in N$_2$ atmosphere was unambiguously confirmed by Mössbauer spectroscopy ($\delta$ = 0.334(2) mm/s; $\varepsilon$ = -0200(1) mm/s, $B$ = 51.01(2) T, Fig.2.) and XRD (Suppl. 4).
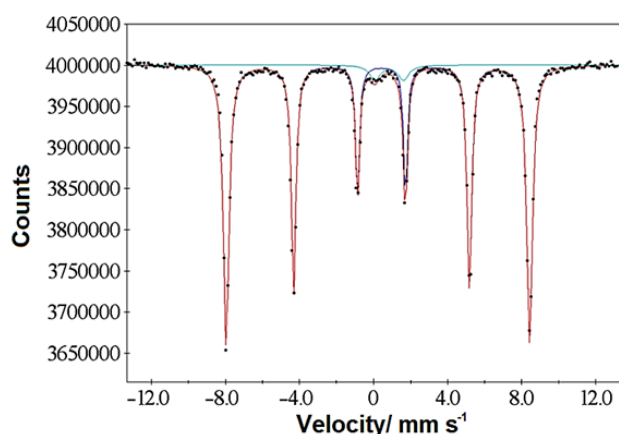
Figure 2. Mössbauer spectrum of the thermal decomposition product of compound **1** at 800 °C under $N_2$ stream

Despite the inert atmosphere and the presence of reducing sulfur(IV) species, the Mössbauer study showed only 3.5 % and 4 % of iron(II) in the decomposition intermediate (Suppl.5a and 5b) and in the final decomposition product at 800 °C, respectively (for this latter: $\delta$=0.85(2) mm s$^{-1}$; $\Delta$=1.55(3) mm s$^{-1}$, Fig.2). Thus, the expected redox reaction between the oxidizing central iron(III) and reducing ligand (sulfite) has no key role in the decomposition. For this minor iron(II) species, the low isomer shift may indicate lower coordination (e.g., 4-coordinate iron) or coordinated sulfur instead of oxygen.

**Table 2.** Thermal decomposition of compound **1** under Ar and air atmosphere (5 K min$^{-1}$ heating rate).

| Stage | Temp. range./ °C | Peak temp./ °C | | Mass loss/ % | MS fragments |
|---|---|---|---|---|---|
| | DTG | DTG | DSC | | |
| Inert atmosphere | | | | | |
| 1 | 99.5-222 | 157.7 | 162.8 | 60.19 | $SO_2$, $S_2$, $NH_3$, $H_2O$, $NO$, S, $N_2$ |
| 2 | 502-606 | 550.4 | merged to the main peak | 12.81 | |
| | | 591.3 | 593.1 | | |
| Air | | | | | |
| 1 | 104-241 | 158 | 161.6 | 55.61 | $SO_2$, $S_2$, $NH_3$, $H_2O$, $NO$, $N_2O$, $H_2S$ |
| 2 | 522-607 | 556 | 558.3 | 14.85 | |
| | | 593 | 594.5 | | |

The thermal decomposition of the compound **1** has two main stages. (*i*) At least three decomposition processes are superposed by heating both under an inert atmosphere and in air. Starting from about 100 °C crystalline water is lost. The DTG peak temperatures are centered around 130, 160 and 207 / 225 °C (under Ar / in air). These decomposition phases could not be separated. and the total mass loss of this stage is 60.19 / 55.91 % in Ar and air, respectively. The mass loss in the second decomposition stage was found to be 12.81 % in inert atmosphere, and 14.85 % in air. As the formula weight of $(NH_4)_2Fe(OH)(SO_3)_2 \cdot H_2O$ is 287 g/mol, it corresponded to only ~37 / ~42 g of lost gases from one mole of the title compound in Ar / air, respectively**.** This demonstrates the non-stoichiometric and/or multiphase composition of the intermediate reaction products formed in the first heating stage. The gas-phase composition monitoring by MS during the thermal decomposition of compound **1** showed almost the same main gaseous decomposition products (sulfur dioxide, water, and ammonia) in both experiments (Figs.3, 4 and 6, Table 2).
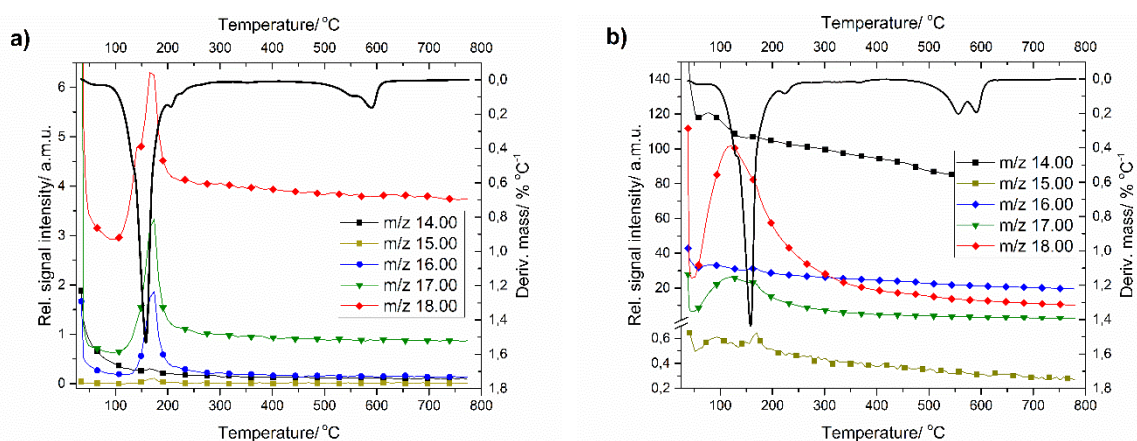
Figure 3. DTG curves and TG-MS ion intensities for $H_2O$ and $NH_3$ -containing products formed during thermal decomposition of compound **1**. a) under Ar, b) under air

Dehydration is performed in at least two consecutive steps; one results from the crystalline water (~130 °C), the other from the hydroxyl group (~170 °C). Some amount of water was formed during the oxidation reaction of ammonia in air (m/z = 30 (NO) and m/z = 44 ($N_2O$)). A larger amount of $N_2O$ was formed from the ammonium ion containing basic iron sulfate intermediates around 480 °C: the oxidic iron compound probably catalyzed the aerial oxidation of the ammonia or the ammonium ion[7]. The mechanism of $NH_3$ oxidation differs in experiments performed under the inert atmosphere and in the presence of air. There is no $N_2O$ evolution under the inert atmosphere, but NO (m/z = 30) and $N_2$ (m/z = 28) formation could be detected. The oxidant in the inert atmosphere might be iron(III)-oxide compounds which could be responsible for the formation of the small amount of iron(II) that was present in the final decomposition product.
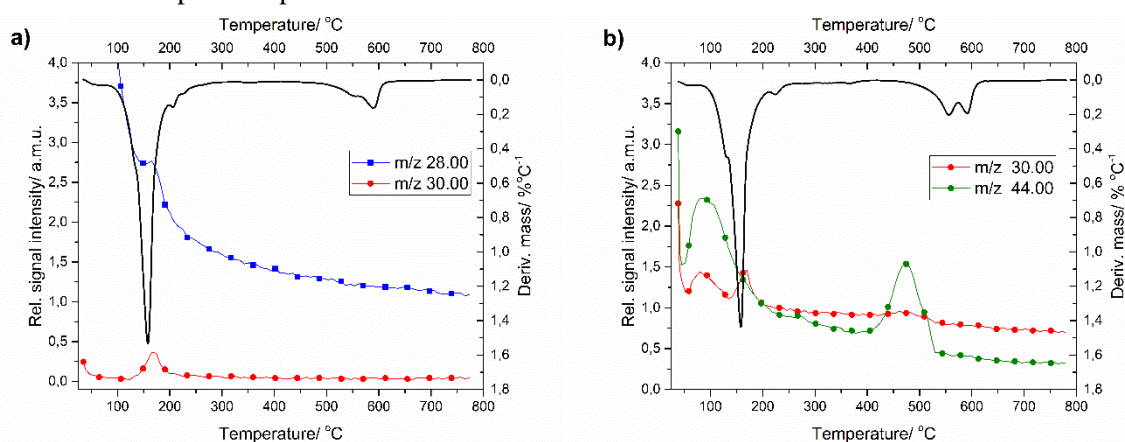


Figure 4. DTG curves and TG-MS ion intensities for $NH_3$-oxidation products formed during thermal decomposition of compound **1**: (a) under Ar; (b) under air

The solid decomposition intermediates and a white sublimate were studied by IR, XRD and Raman techniques. These intermediates and sublimate were obtained after isotherm heating of the compound **1** in air or $N_2$ in a quartz tube at 300 °C. In the iron-containing intermediates, the presence of sulfates and elementary sulfur could be verified (Figs. S6 and S7). A ~6:1 mixture of ammonium sulfite and ammonium sulfate was found in the sublimate (Figs. S8 and S9). These reaction products are an unambiguous evidence for an auto-redox process with a partial oxidation and reduction of the sulfite ions. Since the iron(III) ion is not involved in this redox reaction, the appearance of redox products could only be attributed to the disproportionation of the ammonium sulfite. As a result, ammonium sulfate besides at least one compound containing sulfur with less than four valence, probably an ammonium salt of $H_2S_nO_m$ (n=2-6, m=3-6) acids [13] (Fig. 5). However, the primarily formed sulfur-containing species could easily transform into other species, *e.g.*, into elementary sulfur. The S-containing ions/molecules with intermediate oxidation states showed in Fig. S7 could disproportionate (reduce or oxidize) with the formation of a species with a higher (towards to the left) and another one with a lower (towards to the right) oxidation number. As it could be seen from Fig. 5, the primary disproportionation products of sulfites like thiosulphate or trithionate might also decompose further again into sulfur(IV) compounds (formation as $SO_2$) and with the formation of even lower oxidation compounds (compound located at right).

It is well-known that sulfites could disproportionate into sulfates and sulfides; for example, sodium sulfite and pyrosulfite decompose with disproportionation into sodium sulfate and sodium sulfide around 170°C without mass change [13, 14]. Transition metal sulfites also decomposed into the

appropriate sulfide and sulfate mixture even in the presence of air [15], while under $N_2$ iron(II) sulfite gave iron(II) sulfate, magnetite, and $FeS_2$ [16].
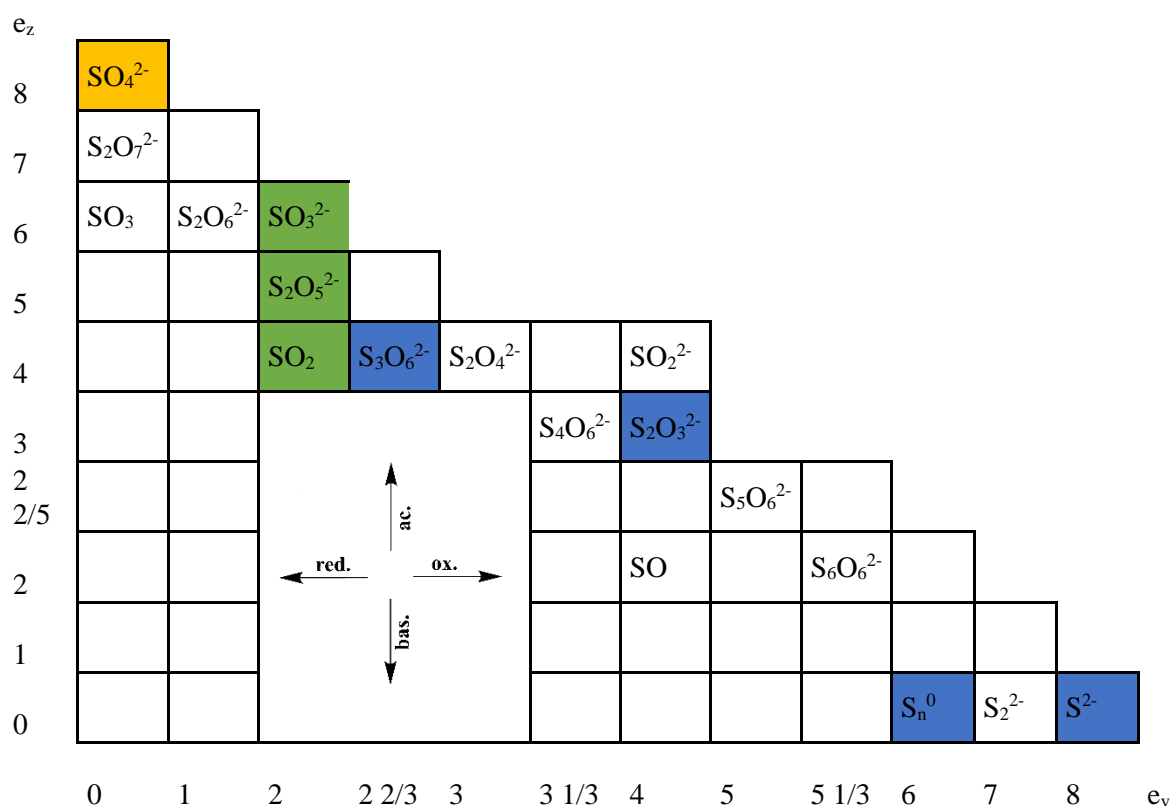


Figure 5. Compilation of sulfur-containing molecules and anion groups that might be formed during the thermal decomposition of **1**. $e_V$ (abscissa): formal number of free electrons normalized to one sulfur atom; $e_Z$ (ordinate): formal number of electric charges normalized to one sulfur atom. Colour codes: green - redox active disproportionating species; yellow - isolable oxidation product; blue - reduced species; light blue - undetectable unstable intermediates; dark blue - neutral molecules or ammonium salts of sulfur-containing acids [13-20]

An analogous reaction of ammonium sulfite formed in the decomposition reaction of **1** could be expected to give ammonium sulfate and ammonium sulfide (Eq. 1). Ammonium sulfate was found in the white sublimate formed during heating. However, ammonium sulfide is not stable and decomposes above room temperature.

$$4(NH_4)_2SO_3 = 3(NH_4)_2SO_4 + (NH_4)_2S \qquad (1)$$

$$(NH_4)_2S = H_2S + 2NH_3 \qquad (2)$$
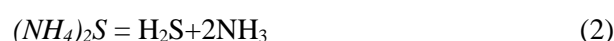
Therefore, only its decomposition products like $H_2S$ and $NH_3$ are detectable (Eq. 2). Accordingly, the evolution of $NH_3$ (m/z = 17 and fragments of it in decreasing intensity at m/z = 16, 15 and 14) were observed on TG-MS both in the air and under the inert atmospheres. The regular decomposition reaction of the compound **1,** however, also results in the formation of $NH_3$. Therefore it was not possible to distinguish between the ammonia formed from $(NH_4)_2S$ or directly from compound **1**. It has to be

mentioned that the peaks of m/z = 17 and 16 contain the contributions of NH$_3$/OH and NH$_2$/O (and double ionized S), while the m/z = 15 exclusive fragments belong to NH$_3$. The peak at m/z = 14 might belong to N atoms or result from NH$_3$ or NO/N$_2$O fragmentations as well. H$_2$S (m/z = 34) was expected as decomposition product. The MS intensities of each fragment origine from different sources are summarized in Table 3.

**Table 3.** Distinctive relative intensities of *m/z* values of analyzed gases according to database available in the mass spectrometer Netzsch QMS 403C and http://webbook.nist.gov/

| *m/z* | Ar/ | SO$_2$ | N$_2$ | NH3 | H$_2$O | N$_2$O | NO | NO$_2$ | H$_2$S |
|------|------|---------|-------|-------|---------|---------|--------|---------|--------|
| 14 | – | – | 7.2% | 2.2% | – | 12.9 % | 7.5 % | 9.6 % | – |
| 15 | – | – | – | 7.5% | – | – | 2.4 % | – | – |
| 16 | – | 11.4% | – | 80.1% | 1.1 % | 5.0 % | 1.5 % | 22.3 % | – |
| 17 | – | – | – | 100% | 23.0 % | – | – | – | – |
| 18 | – | – | – | – | 100 % | – | – | – | – |
| 20 | 20% | – | – | – | – | – | – | – | – |
| 28 | – | – | 100% | – | – | 10.8 % | – | – | – |
| 30 | – | – | – | – | – | 31.1 % | 100 % | 100 % | – |
| 32 | – | 10.4 % | – | – | – | – | – | – | 44.4% |
| 33 | – | – | – | – | – | – | – | – | 42.0% |
| 34 | – | – | – | – | – | – | – | – | 100% |
| 35 | – | – | – | – | – | – | – | – | 2.5% |
| 36 | – | – | – | – | – | – | – | – | 4.2% |
| 40 | 100 % | – | – | – | – | – | – | – | – |
| 44 | – | – | – | – | – | 100 % | – | – | – |
| 46 | – | – | – | – | – | – | – | 37.0 % | – |
| 48 | – | 49.3 % | – | – | – | – | – | – | – |
| 64 | – | 100% | – | – | – | – | – | – | – |

However, it was not detected during heating experiments in inert atmosphere; in air traces of HS (m/z = 33) and H$_2$S (m/z = 34) were detected. Since H$_2$S immediately could react with the large amount of SO$_2$ resulting in the formation of elementary sulfur, the S$_n$ (n = 1-8) species and other gaseous sulfur variants [17] should be monitored instead.
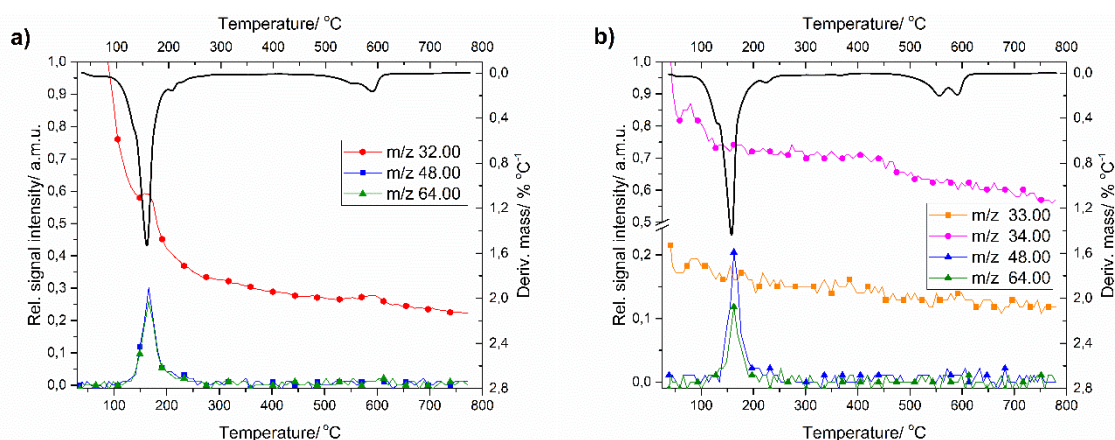


Figure 6. DTG curves and TG-MS ion intensities for S-containing products formed during thermal decomposition of compound **1** under Ar (a), under air (b).

Accordingly, a signal at m/z = 64 may belong to $SO_2$ and $S_2$ as parental species; also SO (m/z = 48) and monoatomic S (m/z = 32) as fragment ions of $SO_2$ and $S_2$, respectively, could be detected. In air m/z = 32 could not be allocated to any reaction product due to the complete overlap with of aerial $O_2$. The ratios of the signal intensities resulting from the components $SO_2+S_2$ (m/z = 64) and SO (m/z = 48) in air and inert atmosphere, respectively, differ: *i.e.*, $I_{64}/I_{48}$ was found to be ~1 under argon but it was <<1 in air. It could be attributed to the distinct amount of $SO_2$ and $S_2$ formed in the air and under the inert atmosphere. SO was supposed to originate exclusively from the fragmentation of $SO_2$. As the fragmentation obviously is independent on the distinct atmosphere, the $SO_2$/SO ratio might be attributed to a decrease of $S_2$ accompanied by an increase of $SO_2$ contributing to the intensity of the m/z = 64 peak (oxidation of $S_2$ in the air results into the formation of $SO_2$). Actually, $S_2$ was detected at the temperatures close to the decomposition temperature (170 °C) of the compound **1** [17].

The overall decomposition process is very complex due to the reaction of the intermediate products ammonia, sulfur dioxide, and water forming ammonium sulfite. In this reaction, the formation of ammonium sulfite was always accompanied by the formation of some amounts of ammonium thiosulphate and elementary sulfur [18]. Ammonium thiosulfate itself decomposes into $NH_3$, $SO_2$, hydrogen sulfide, and ammonium trithionate at 150 °C at low heating rates (Eq. 3); during fast heating $NH_3$, S, and ammonium sulfate are formed [20]. The ammonium trithionate also decomposes at 160-170 °C forming of analog reaction products [19].

$$(NH_4)_2S_2O_3 = 2\,NH_3 + H_2S + (NH_4)_2S_3O_6 \qquad (3)$$
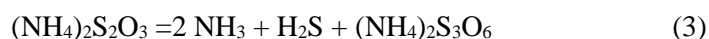
Since the decomposition temperatures of ammonium thiosulphate, trithionate and other polythionates are within the range of that of compound **1** (~150-170 °C), only the decomposition products (S, $SO_2$, $H_2S$, $NH_3$) of these possible intermediate compounds could be observed. Raman spectra of solid iron-containing intermediates confirm the presence of sulfur (Fig. S10). The three most intense absorption bands are allocated to $S_n$ species [22]; they occur at 143 ($\nu_8$, e, torsion), 218 ($\nu_2$, $a_1$, bending) or 484 ($\nu_1(a_1)$ and $\nu_7(e_2)$, stretching) cm$^{-1}$ in both cases. The summarized possible reaction routes are presented in Fig. 7.
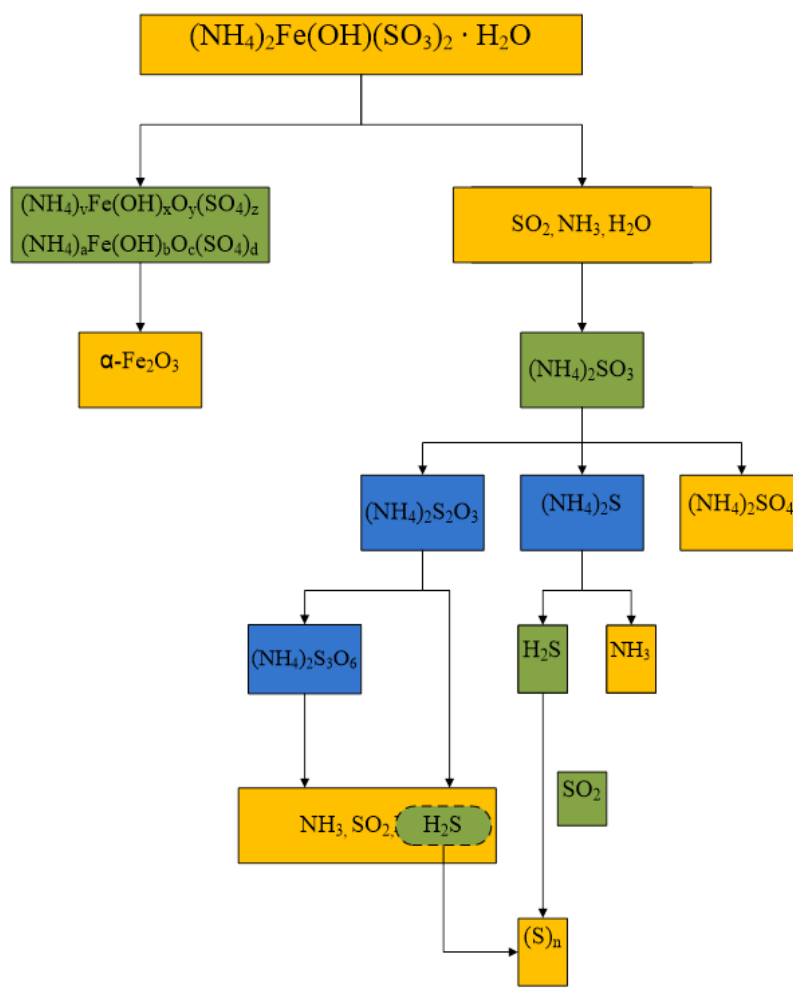
Figure 7. The supposed decomposition routes of compound **1**. Green: redox active and disproportionating species; yellow: isolable products; blue: non-isolable reduced species.

*The chemical nature of solid intermediates*

Two types of intermediates were formed during the thermal decomposition of compound **1** both in air and in inert atmosphere; *i.e.*, an iron-containing residue and a sublimate containing an ammonium sulfite and an ammonium sulfate. The Mössbauer spectra of the former intermediate (Fig. S5) showed the presence of two iron(III) environments in a ~3:1 and ~3:2 ratio for the experiments under $N_2$ and air; the iron to sulfur atomic ratio was 2.15:1 and 1.25:1, respectively, as detected by ICP measurements. These intermediates were supposed to be a two-component mixture of basic iron sulfate compounds; at least one of them must contain ammonium ions as well. The different ratios reflect the distinct atmospheres. Since the presence of oxygen is proposed to oxidize $SO_2$ formed during the first decomposition step in the presence of iron oxides [7], a larger amount of sulfur might be retained as sulfate in the sample investigated under air. Thus, the amount of the sulfur-rich iron sulfate phase must be higher as compared to the decomposition under the inert atmosphere. Therefore the Mössbauer doublet with $\delta = 0.34$ mm s$^{-1}$ and $\Delta = 1.34$ mm s$^{-1}$ and the lower decomposition temperature on the DTG curve (~550°C) might belong to the component richer in sulfur than the component decomposed at 600 °C which gave Mössbauer parameters $\delta = 0.36$ mm s$^{-1}$ and $\Delta = 0.81$ mm s$^{-1}$.

The intensity change of the DTG/DSC signal components at 550/600 °C under Ar and air confirmed the different amounts of the two basic iron sulfates (the Mössbauer and IR characteristics for the intermediates (Table 4) were proved to be almost the same for the two atmospheres ).
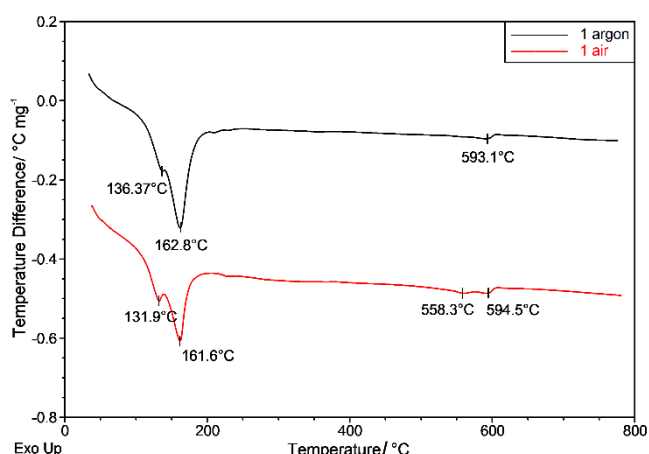


Figure 8. DSC curves (simultenous measurement with TG) of compound **1** in air and under Ar

Numerous basic ammonium iron sulfate compounds like ammonium jarozites are known with similar IR, Mössbauer and thermal decomposition characteristics as we found in the case of the intermediates formed in our experiments [8,9,12].

Table 4. Wavenumbers of the IR bands of decomposition intermediates of compound **1**.

| Assignation | IR/ cm$^{-1}$ | relative intensity | IR/ cm$^{-1}$ | relative intensity |
|---|---|---|---|---|
| | **Reaction under air** | | **Reaction under N$_2$** | |
| $\nu_1$ and $\nu_3$ (NH)+$\nu$(OH) | 3380 | 0.44 | 3380 | 0.26 |
| $\nu_3$ (NH) | 3228 | 0.43 | 3228 | 0.29 |
| $\nu_1$(A$_1$) (NH) | 3072 | 0.43 | 3075 | 0.28 |
| 2$\nu_4$ (NH) | 2860 | 0.41 | 2859 | 0.25 |
| $\nu_2$(E) (NH) or $\delta$(OH) | 1633 | 0.40 | 1632 | 0.25 |
| $\nu_4$ (F$_2$) (NH) | 1431 | 0.43 | 1427 | 0.30 |
| $\nu_3$(F$_2$) (SO) | 1183 | 0.50 | 1196 | 0.36 |
| $\nu_3$(F$_2$) (SO) | 1045 | 0.611 | 1034 | 0.53 |
| $\nu_1$(A$_1$) (SO) or $\delta$(OH$_{bridge}$) | 991 | 0.57 | 998 | 0.50 |
| $\nu_4$(F$_2$) (SO) | ~650 | shoulder | ~650 | shoulder |
| $\nu_4$(F$_2$) (SO) | 595 | 0.64 | 587 | 0.49 |
| $\nu_2$(E) (SO) | ~450 | 0.73 | ~450 | 0.53 |

The intermediates showed the presence of a bridged sulfate and a rotation-hindered ammonium ion. The appearance of the tentatively assigned $\nu_1$+$\nu_5$ combination band ($\nu_5$ is a far-IR lattice band) is characteristic for a basic ammonium iron compound with polymerized sulfates and strong hydrogen bonds between the ammonium and oxide/sulfate ions. The absorption bands resulting from a bridging/complexed hydroxy group might be located at 970 to 1000 and 1100 cm$^{-1}$ overlapping with the absorption bands of the sulfate ions. The absorption band around the $\delta$(OH) deformation band (1650 cm$^{-1}$) is close to the $\nu_2$(NH) absorption band; the upper combination bands might overlap with $\nu$(OH) as well.

There was an important difference between the decomposition intermediate of the pure **1** (synthesized during the present work) and the contaminated sample (**1a**) prepared according to Erämetsä and Valkonen [3]. The decomposition of compound **1a** at 300 °C (2 h, N$_2$ atmosphere) resulted in two crystalline phases which could be identified as NH$_4$Fe(SO$_4$)$_2$ (**2**) and (NH$_4$)$_3$Fe(SO$_4$)$_3$ (**3**) by XRD (Fig. S4). The IR spectra of the intermediates from compound **1** taken under analogous conditions were very similar indicating that both materials contain ammonium and sulfate ions in similar chemical environments as in compounds **2** and **3**. However, the Mössbauer spectra (taken under air or N$_2$) obtained from the decomposition intermediates from compound **1** and those from compounds **2** and **3** (synthesized according to [10] and [11]) are quite different. Neither compound **2** nor **3** are formed during decomposition of compound **1**. The decomposition temperatures of the compounds **2** and **3** are roughly around 400 and 500 °C, respectively [7]. There was no decomposition step of the pure compound **1** at these temperatures. Thus, the compound **2** and **3** formed probably by a decomposition reaction of an unknown contaminant present in the impure sample (**1a**) prepared by the original method given by [3].

**Conclusions**

1. The thermal decomposition of ammonium hydroxodisulphitoferriate(III), (diammonium *catena*-{bis($\mu^2$-sulfito-O,O)-$\mu^2$-hydroxo-}ferrate(III) monohydrate), $(NH_4)_2[Fe(SO_3)_2OH]\cdot H_2O$, is a two-stage (chemically multistep within each thermal decomposition stages) process with formation of two basic ammonium iron sulfate intermediates, whose relative amount differs for the samples prepared in an oxidizing or inert atmosphere.

2. The first decomposition stage is located between 100 and 240 °C, the primary decomposition release $SO_2$, $NH_3$ and $H_2O$, which form isolable ammonium sulfite intermediates in spite of the expected redox reaction between the iron(III) and sulfite ions. Only a marginal amount of iron(II) ions is formed (ca. 3.5-4 mol%). During the decomposition in an inert atmosphere, the final decomposition product is $\alpha$-$Fe_2O_3$ (mineral name hematite).

3. The ammonium sulfite formed from $SO_2$, $NH_3$ and $H_2O$ at the first decomposition step of **1** disproportionates, leading to the formation of ammonium sulfate and an unstable ammonium sulfide. The latter releases upon decomposition and reaction with $SO_2$ elementary sulfur. The sulfur formation may take place in parallel with the decomposition of further by-products/intermediates such as ammonium thiosulphate or trithionate. These processes are superposed into one decomposition stage. The mass loss in the second decomposition stage is 12.81 % in the inert atmosphere, and 14.85 % in air.

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